Phenol Formaldehyde COO...

PROPERTIES OF PHENOL FORMALDEHYDE WITH THREE FILLER TYPES

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ABSTRACT

A filler is needed in the glue-mix to improve its properties for wood-to-wood bonding. Filler's characteristics influence the behavior of an adhesive-mix in producing the secondary bonding forces in the glueline.

The properties of phenolic adhesive filled with three filler types were studied. Three factors were used in developing glue-mix for completing the adhesive behavior. They were agitation time, particle size class and drying condition.

Agitation time caused glue-mix viscosities varied. A prolonged agitation time developed higher viscosity. Particle size class showed the same effect to agitation time, wherein finer particles produced higher glue-mix. Drying condition showed a different result compared to the first two factor's effect. Glue-mix viscosity was affected by filler type. Tea waste showed its more hydrophilic characteristics than kemiri shell and white clay by developing higher glue-mix viscosity.

INTRODUCTION

A filler is a substance added into a synthetic resin adhesive to improve the desired glue-mix properties for wood-to-wood bonding. It constitutes as one of the several important ingredients which are mixed in a certain adhesive formulation following its respective procedure depending on its purpose. The chemical constituents such as moisture content, ether extract content, crude fiber content and ash content of a filler influence the behavior of an adhesive-mix thereby affecting the reactivity of wood fibers and other structural components of wood veneer substrates in producing the secondary bonding forces in the glueline. The quantity of adhesive-mix molecules that strike through into the tracheids, rays, vessels and other possible liquid passages is governed by the glue-mix properties in addition to the response of physical and chemical properties of the substrates. Logically the quantity of adhesive-mix molecules retained at the glueline depend on the substrate's characteristics and they adhesive-mix qualities.

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Generally, the viscosity of the glue-mix is used to detect the degree of polymerization reaction within the pot life of the adhesive-mix. Certain ingredient of a glue-mix is capable to influence the viscosity behavior due to different qualities and magnitude of a substance added into the adhesive system. Catalysts, hardeners, extenders and fillers are perceived to be capable to fluctuate and make the undue viscosity behavior of the glue-mix. Those substances earn their qualities through firstly, inherent characteristics materials that can distinguish them from one to another; secondly, through several and/or type of phases of substance manufacturing. Particle size and classes, drying condition and agitation time in the resin adhesive preparation are among those factors that affect the adhesive quality.

In the light of the problems presented above, this paper will discuss the property of phenol formaldehyde adhesive with three filler types.

REVIEW OF LITERATURE

Filler Characteristics Affecting Glue-mix Qualities

Several factors are known to influence the glue-mix quality. They consist of inherent factors in each ingredient of the glue-mix and the various factors when they are mixed together. Ingredients such as filler, extender, catalyst, hardener and the resin itself exert their characteristics and contribute significantly to the resultant behavior of the glue-mix.

Filler properties play major role in affecting glue-mix viscosity. Viscosity is defined as the frictional resistance of liquid to flow when that resistance is directly proportional to the applied force. The viscosity of the glue-mix decreases with the rise in temperature which has an effect on the dispersion medium. Water which is generally the dispersion medium has viscosities of 0.28 and 1.79 cps at 100°C and 0°C respectively. This contributes a significant drop of glue-mix viscosity when the gluelines are heated to cure the adhesive.

Viscosity changes in adhesive system is affected by the addition of inert materials that attract water molecules out from resin dispersion medium thus produce an viscosity increase. High water taking capability of the inert material induces water starvation which results a sudden increase in adhesive-mix viscosity (Robertson and Robertson, 1977). Agitation is an effort to obtain a complete blending of filler and adhesive molecules, thus facilitating fine contact between them and producing high bonding among ingredient molecules of the adhesive system.

The mobility of glue-mix molecules is in reciprocal function of the glue's viscosity, which means high viscosity produces low glue molecules mobility and vice versa. This reduced mobility of adhesive-mix molecules can promote a better bond formation and higher bond strength. Sullivan and Harrison (1965) proved this by measuring the viscosity development of walnut shell filled RF glue-mix and then compared it to the unfilled one.

Filler's Properties Related to Bond Formation

Skeits (1962) defines a filler as a relatively non adhesive substance added to an adhesive system to improve working properties, permanence strength and other qualities. The proposed material for filler should be capable to provide a frame-body to counteract the incoming pressure during the adhesive setting period and in the adhesive quality control test such as hot and cold and boiling cycle test as well. Therefore an inert material is the possible appropriate material that fulfill the said requirements.

Glueline thickness is an important subject matter to be taken into account in bond formation. The thicker glueline, the lower the bond strength and vice versa. Filler particle size can logically assist in producing the required glueline thickness. The finer particle size will be likely to develop thin glueline thus producing higher bond strength due to the obtained intimate contact of the adherends (Rice, 1965).

High fibrous materials are preferred in filler selection because the high possibility of autohesion forces development among filler particles. On the other hand, the adhesion forces that are expected to occur at the interfaces of the filler substances and pure resin adhesive molecules are influenced by the presence of fatty acids and resin acids in the fillers. The lower content of those substances promotes high adhesion strength between adhesive and filler molecules. The only filler property that affects the abrasiveness of the glueline is filler's ash content. Therefore high ash content in the filler is avoided (Robertson and Robertson, 1977).

MATERIALS AND METHODS

Materials

Three filler types were used in the study, namely white clay, kemiri shell and tea waste. White clay was obtained from Pegunungan Seribu, Seputih village, Kenteng, Nanggulan, Kulon Progo District of Yogyakarta. Kemiri seeds were procured from Wanagama, a special forest district for educational purposes of the Faculty of Forestry GMU, Yogyakarta. The fallen seeds were collected from trees that have just passed their fruiting season. Tea waste as the third filler was supplied by PT Pagilaran of the Faculty of Agriculture GMU, Yogyakarta as a still unused commercial black tea-leaves.

Experimental Design

Factorial experiment in CRD of 3 × 3 with three replicates was employed in analyzing the glue-mix viscosity. Tukey's w mean comparison was used in detecting the significant effect among treatment means, coupled with the use of partitioning the sum of squares when it was necessary.

RESULTS AND DISCUSSION

Agitation Time Effect

The viscosity of phenolic glue-mixes formulated by three filler types and agitation time are shown in Table 1, while Table 2 summerizes its analysis of variance and Table 3 expresses the Tukey-w mean comparison. All factors involved and their combination were highly significant. Tea waste filled phenolic glue-mix showed the highest viscosity of 67.14 poise, while kemiri shell and white clay filled one were 10.55 and 6.68 poise respectively. This result proves that white clay filler possesses a low water adsorbing capability thereby allowing water molecules to exist in dispersion medium thus producing low viscosity. On the other hand tea waste has almost adsorbed all water molecules available in the adhesive system thus resulting to a sudden viscosity increase. Kemiri shell shows its intermediate.

Agitation time factor expressed its significant effect on glue-mix behavior. Generally, longer agitation time promotes an increase in viscosity. The glue-mix viscosity of T1, T2 and T3 were 23.32; 29.64 and 31.42 poise respectively. Partition of sum of squares showed that T1 significantly different to T2 and T3, while T2 did not differ with T3. This may conclude that an increase of agitation time does not produce a steady increase of viscosity. This might be due to several factors involved in viscosity behavior, such as viscosity increase due to the loss of water to the filler molecules, to high water taking capability and to bigger portion of high molecular weight resin adhesive parallel to advanced polymerization reaction. Tukey-w mean comparison conducted on this viscosity variation revealed that F3 was the responsive filler. Table 2 strenghthens this finding by showing the only F3 (tea waste) behaves differently to the others (F1 and F2). Figure 1 shows the effect of agitation time.

In terms of water filler ratio, white clay showed a very low level of water adsorption taken from the medium dispersion in such extent that a little increase in viscosity observed. On the other hand tea waste behaved in a reverse action, meaning a high level of water adsorption had been observed which was indicated by a sudden increase in viscosity. A water filler ratio is an indication of the affinity of filler molecules to water molecules existing in the dispersion medium. This is strengthened by filler moisture content variation of 3.64%; 8.22% and 9.90% for white clay, kemiri shell and tea waste respectively (Prayitno, 1990). Table 4 andFigure 2 show the water filler ratio of three filler materials under study.

Table 1. **Apparent Viscosities of Phenolic Glue-mix Filled with Three Fillers at Three Agitation Time**

Filler Type, F	Agitation Time, T[a]	Replicate 1	Replicate 2	Replicate 3	Average
F1	T1	6.00	7.10	6.00	6.37
	T2	6.05	6.40	6.60	6.35
	T3	7.40	7.60	7.00	7.33
F2	T1	9.40	9.90	9.50	9.60
	T2	11.00	10.60	10.60	10.73
	T3	12.15	10.80	11.00	11.32
F3	T1	50.50	55.75	55.75	54.00
	T2	70.50	72.40	72.60	71.83
	T3	70.50	77.50	78.80	75.60
Average	F1	6.48	7.03	6.53	6.65
	F2	10.85	10.43	10.37	10.55
	F3	63.83	68.55	69.05	67.14
	F	27.06	28.67	28.65	28.13
	T1	21.97	24.25	23.75	23.32
	T2	29.18	29.80	29.93	29.64
	T3	30.02	31.97	32.27	31.42
	T	27.26	28.67	28.65	28.13

[a]T: T1, T2, T3 are 1-hour, 2-hour, 3-hour agitation time.

Table 2. **Analysis of Variance of Phenolic Glue-mix Viscosities Filled with Three Fillers at Three Agitation Time**

SV	DF	SS	MS	F-Value
F	2	20,626.33	10,313.17	2,905.12**
F3 vs. F1, 2	1	20,551.05	20,551.05	5,789.02**
F1 vs. F2	1	75.28	75.28	21.20**
T	2	325.11	162.55	45.79**
T1 vs. T2,3	1	311.91	311.91	87.86**
T2 vs. T3	1	13.21	13.21	3.72NS
Linear (TL)	1	294.84	294.84	83.05**
Quadratic (TQ)	1	30.27	30.27	8.53**
F × T	4	477.59	119.40	33.63**
F × TL	2	410.82	205.41	57.86**
F × TQ	2	66.77	33.39	9.41**
(F3 vs F1, 2) × TQ	1	64.92	64.92	18.29**
Residual	1	1.85	1.85	0.52NS
Error	18	63.82	3.55	
Total	26	21,492.85		

** Signicantly different at 99% probability level.
NS-Nonsignificantly different at 95% probability level.

Table 3. **Tukey's Means Comparison of Phenolic Glue-mix Viscosities Filled with Three Fillers at Three Agitation Time**

Filler Type, F	Agitation Time			Average
	T1	T2	T3	
F1	6.37c	6.35c	7.33c	6.68r
F2	9.60c	10.73c	11.32c	10.55q
F3	54.00b	71.83a	75.60a	67.14p
Average	23.32y	29.64x	31.42x	28.13

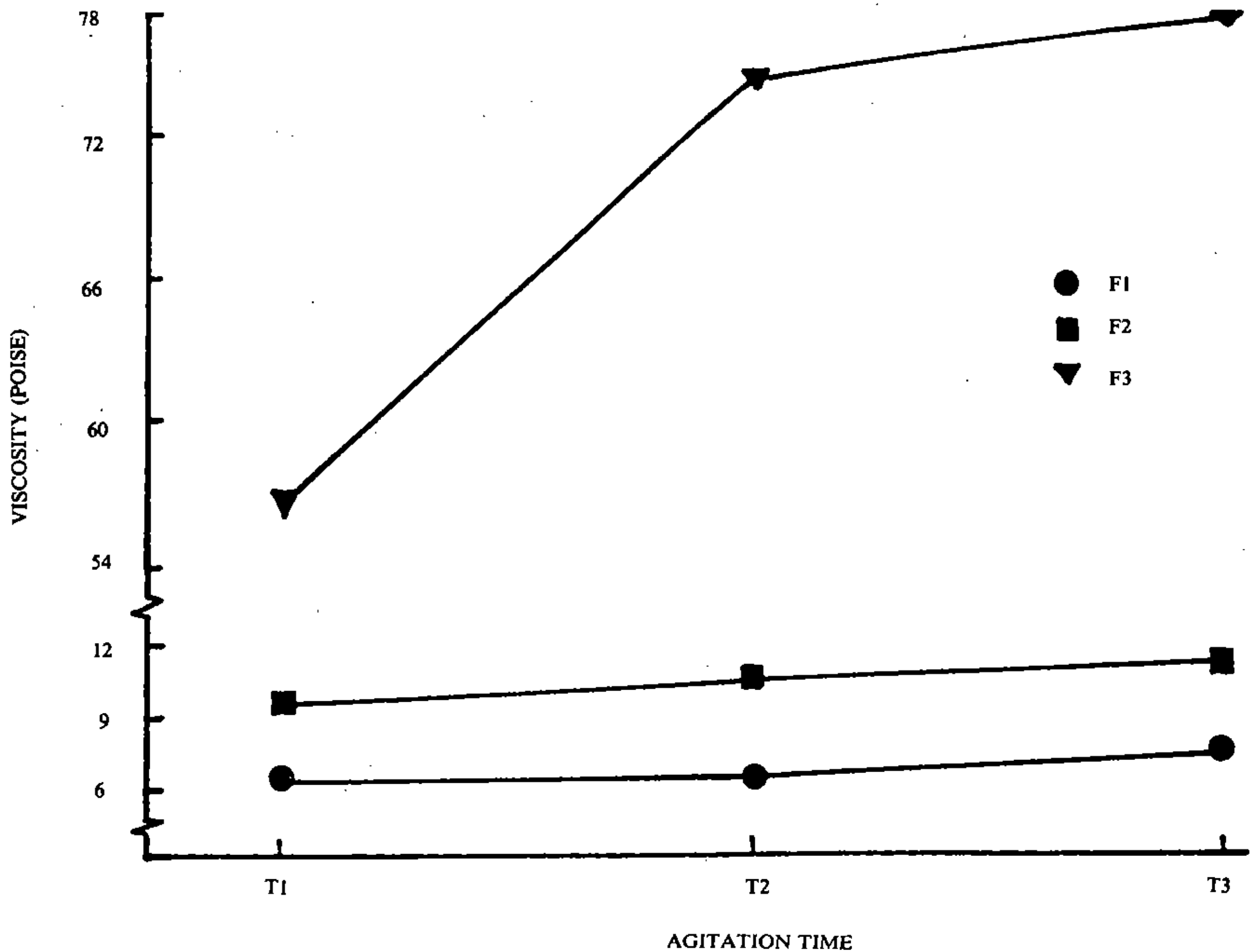

Figure 1. The Effect of Agitation Time on Phenolic Glue-mix Viscosity Filled

Particle Size Class Effect

The apparent viscosity of phenolic glue-mix filled with three filler particle size class is shown in Table 5, while its analysis variance is summerized in Table 6. Table 7 shows mean comparison resulting from the Tukey-w procedure. All sources of variance coming from two factors with their combination showed their significant effect.

Particle size factor showed significant effect among the particle size class, meaning that P1 was significantly different to group of P2 and P3; P2 was significant to P3 as well. Similarly, F3 against group of F1 and F2; and F1 against F2 (Table 6). Finer particles provide more exposed surface area to surrounding air or medium dispersion that can attract more foreign molecules such as water, thus lessen the amount of water molecules in the dispersion of resin system thereby facilitating a viscosity increase. The interaction between filler types and particle size class means that each filler type behaves differently when it is reduced to certain particle size class and then added into a resin adhesive system (Table 7). In the discussion of water filler ratio it is shown that each filler type differs in response to the adhesive system, and then producing different pattern of adhesive-mix viscosity (Figure 1). This variation can be detected in Figure 2.

Drying Condition Effect

The apparent viscosity of phenolic glue-mix filled with three filler types and drying condition is shown in Table 8, while its analysis is summerized in Table 9. Table 10 expresses the mean comparison resulted from Tukey-w procedure. All sources of variance in the experiment showed their significant effect.

Filler types resulted a similar effect in the previous subexperiment, meaning that a decreasing trend of glue-mix viscosity from tea waste to white clay existed as observed in the two previous subexperiment of agitation time and particle size class effect. On the other hand drying condition behave differently when it is compared to the effect of this factor in filler characteristics analysis (Prayitno, 1990). Drying condition of D1 (100°C) produced a different filler characteristics compared to other two and the last two of D2 and D3 produce the same effect. Table 7 showed that D2 was significantly different to D1 and D3, while D1 and D3 was not different to each other. Interaction between filler types and drying condition was significantly caused by the first filler type of while clay (Table 10 and Figure 3).

Table 4. **Apparent Viscosities of Phenol Formaldehyde Adhesive-mix Filled with Three Fillers at 6% Level of Filler's Extension**

F	Water-filler Ratio	Viscosity (Poise)
F1	0.00	7.50
	0.05	7.20
	0.10	7.00
	0.33	6.50
	0.50	5.50
F2	0.00	11.50
	0.10	11.50
	0.50	9.00
	0.75	8.60
	1.00	7.40
	1.11	6.90
	1.22	6.50
F3	0.00	45.50
	0.11	45.50
	0.50	33.50
	0.75	28.50
	1.00	24.50
	1.39	19.00
	1.78	15.00
	2.39	10.00
	2.89	7.50
	3.22	6.50

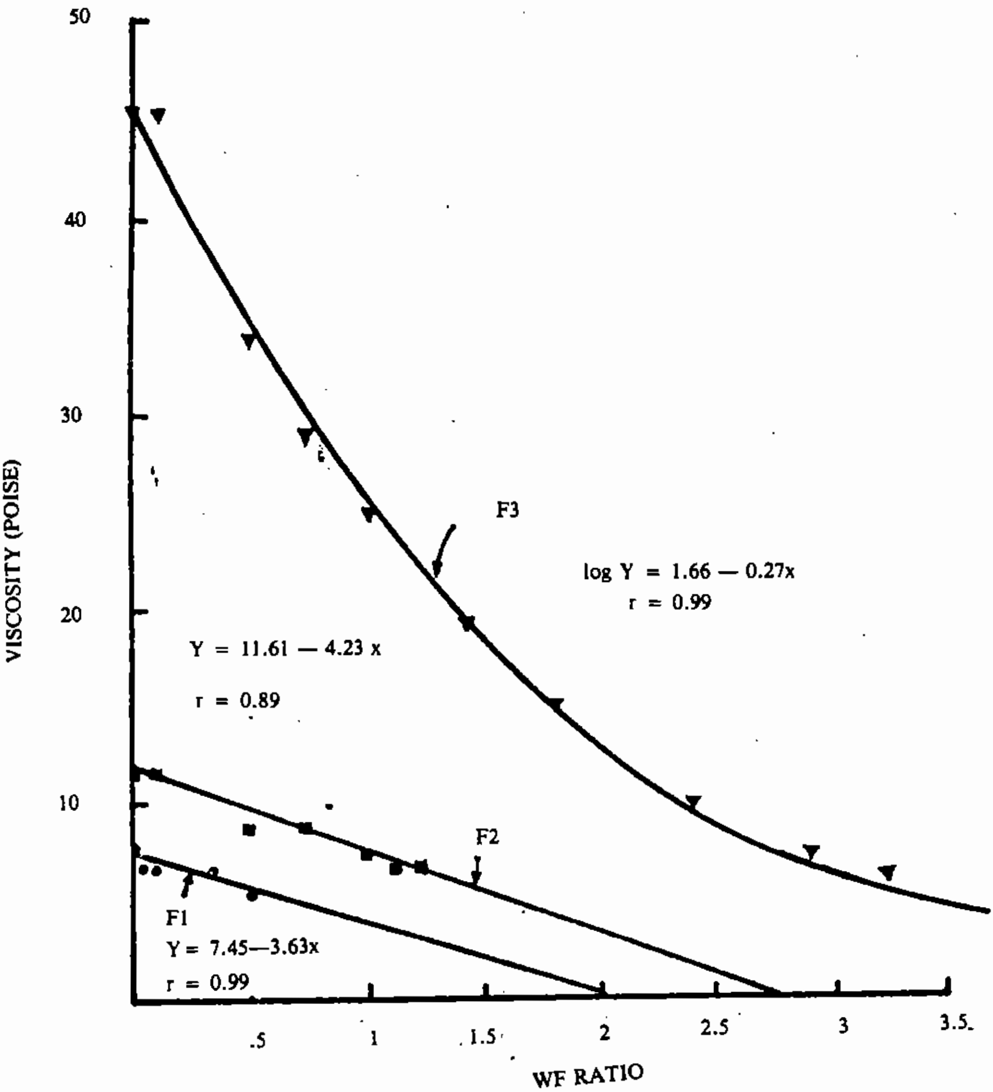

Figure 2. **Relationship of Apparent Viscosities of Phenol Formaldehyde Glue-mix Filled with Three Fillers to Their Water Filler (WF) Ratios**

Table 5. Apparent Viscosities of Phenolic Glue-mix Filled with Three Fillers of Three Particle Size Classes

Filler Type, F	Particle Size Class, P	Replicate 1	Replicate 2	Replicate 3	Average
F1	P1	10.00	11.10	10.00	10.37
	P2	10.50	10.40	11.25	10.72
	P3	11.90	11.10	11.10	11.37
F2	P1	17.50	16.00	17.50	17.00
	P2	18.05	20.10	20.00	19.38
	P3	21.50	21.40	19.90	20.93
F3	P1	50.00	55.00	54.50	53.17
	P2	56.40	61.25	61.50	59.72
	P3	62.40	66.00	66.25	64.85
Average	F1	10.80	10.87	10.78	10.82
	F2	19.02	19.17	19.13	19.10
	F3	56.27	60.75	60.75	59.25
	F	28.69	30.26	30.22	29.72
	P1	25.83	27.37	27.33	26.85
	P2	28.32	30.58	30.92	29.94
	P3	31.93	32.83	32.42	32.38
P	28.69	30.26	30.22	29.72	

Table 6. Analysis of Variance of Phenolic Glue-mix Viscosities Filled with Three Fillers of Three Particle Size Classes

SV	DF	SS	MS	F-Value
F	2	12,084.12	6,042.06	2,237.80**
F3 vs. F1,2	1	11,768.62	11,769.62	4,359.12**
F1 vs. F2	1	314.50	314.50	116.48**
P	2	139.56	69.78	25.84**
P1 vs. P2,3	1	111.46	111.46	41.28**
P2 vs. P3	1	28.10	28.10	10.41**
F × P	4	93.04	23.26	8.61**
Error	18	48.64	2.70	
Total	26	12,365.36		

Table 7. **Tukey's w Mean Comparison or Phenolic Glue-mix Viscosities Filled with Three Fillers of Three Particle Size Classes**

Filler Type, F	**Particle Size Class, P**			**Average**
	P1	**P2**	**P3**	
F1	10.37f	10.72f	11.37ef	10.82r
F2	17.00de	19.38d	20.93c	19.10q
F3	53.17b	59.72a	64.85a	59.25p
Average	36.85z	29.94y	32.38x	29.72

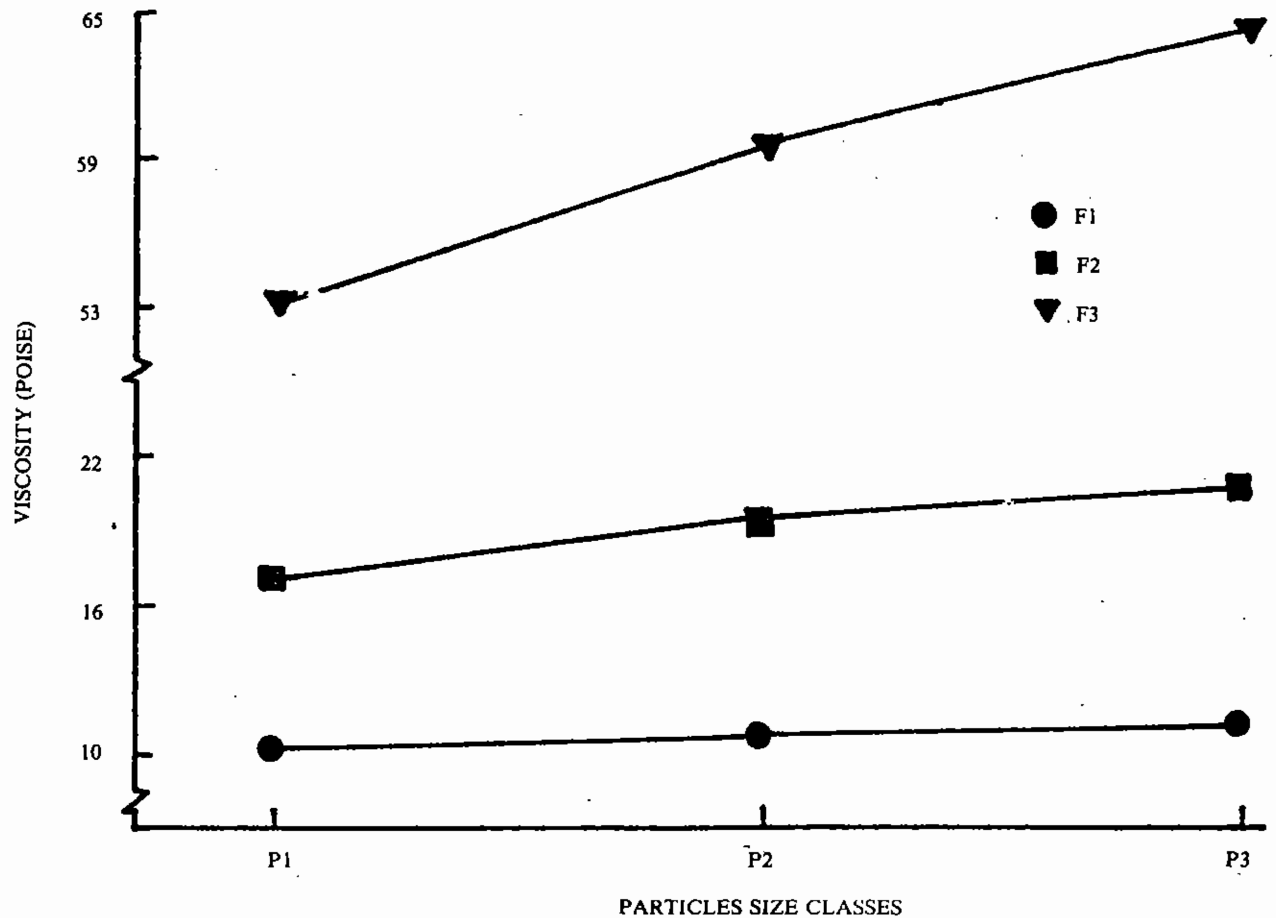

Figure 3. The Effect of Particle Size Classes on Phenolic Glue-mix Viscosity Filled with Three Filler

Table 8. **Apparent Viscosities of Phenolic Glue-mix Filled with Three Fillers of Three Drying Conditions**

Filler Type, F	Drying Condition, D	Replicate 1	Replicate 2	Replicate 3	Average
F1	D1	11.50	11.10	11.25	11.28
	D2	10.00	9.00	10.10	9.70
	D3	10.10	11.00	10.00	10.37
F2	D1	12.95	13.25	13.50	13.23
	D2	9.40	8.50	9.50	9.13
	D3	17.50	15.00	17.50	16.67
F3	D1	56.10	57.50	57.85	57.15
	D2	43.40	47.50	47.10	46.00
	D3	54.50	52.50	54.50	53.73
Average	F1	10.53	10.37	10.45	10.45
	F2	13.28	12.25	13.50	13.01
	F3	51.33	52.50	53.15	52.29
	F	25.05	25.00	25.70	25.25
	D1	26.85	27.17	27.53	27.22
	D2	20.93	21.67	22.23	21.61
	D3	27.37	26.07	27.33	26.92
	D	25.05	25.00	25.70	25.25

Table 9. **Analysis of Variance of Phenolic Glue-mix Filled with Three Fillers of Three Drying Conditions**

S V	DF	SS	MS	F-Value
F	2	9,900.87	4.950.44	4,091.27**
F3 vs. F1,2	1	9,870.68	9,870.68	8,157.59**
F1 vs. F2	1	30.19	30.19	24.95**
D	2	180.14	90.07	74.44**
D2 vs. D1,3	1	178.87	178.87	147.83**
D1 vs. D3	1	1.27	1.27	1.05NS
F × D	4	105.42	26.35	21.78**
Error	18	21.86	1.21	
Total	26	10,208.28		

** Significantly different at 99% probability level

NS = non-significantly different at 95% probability level.

Table 10. **Tukey's w Means Comparison of Phenolic Glue-mix Filled with Three Fillers of Three Drying Conditions**

Filler Type, F	**Drying Condition, D**			**Average**
	D1	**D2**	**D3**	
F1	11.28de	9.70de	10.37de	10.45r
F2	12.23cd	9.13c	16.67c	13.01q
F3	57.15a	46.00b	53.73a	52.29a
Average	27.22x	21.61y	26.92x	25.25

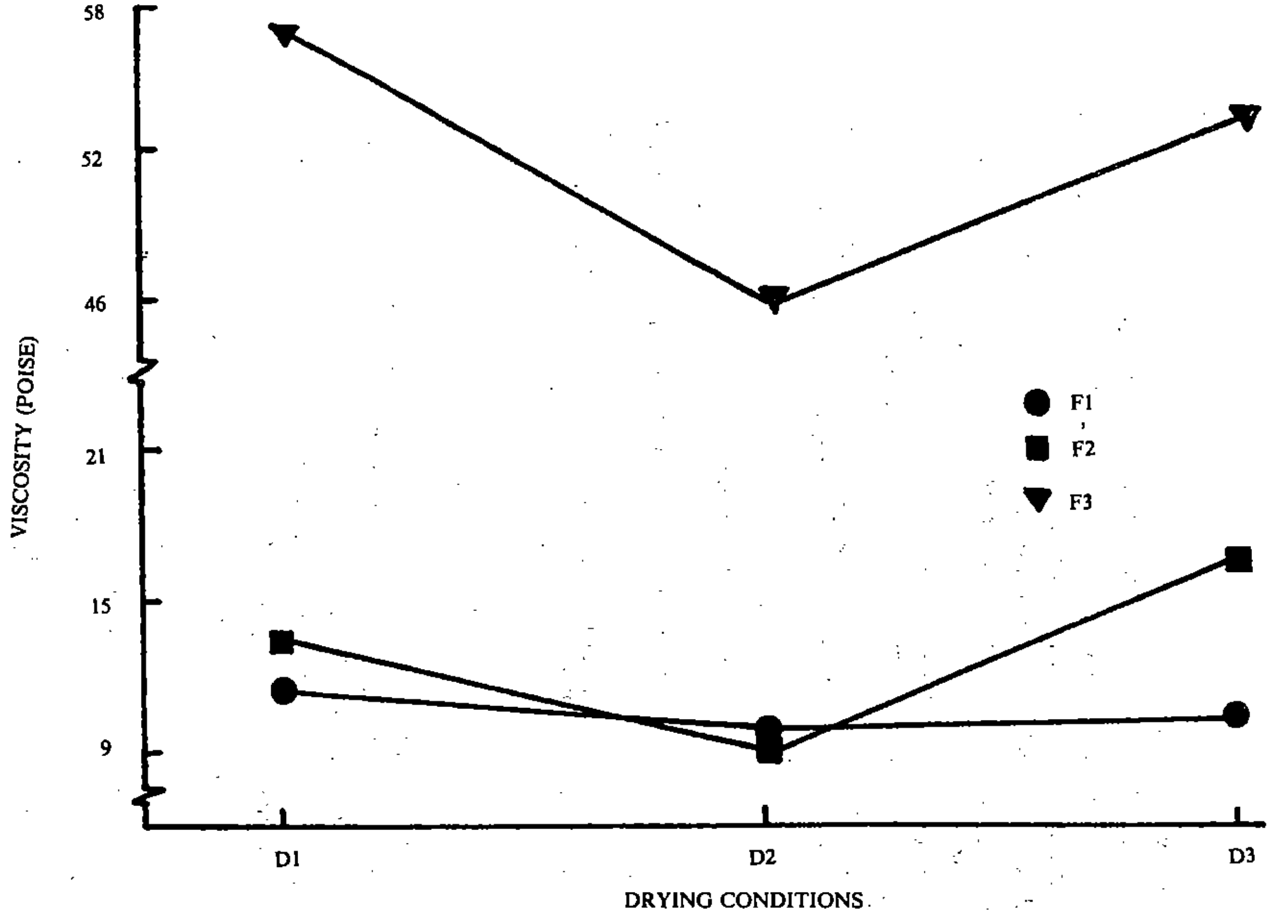

Figure 4. The Effect of Drying Conditions on Glue-mix viscosity of Three Different Types of Fillers

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The study has produced some findings that are expected to contribute significantly to the field of wood adhesion as the following:

1. Agitation time causes phenolic glue-mix viscosities varies. A prolonged agitation time develops higher viscosity.
2. Particle size class brings about different glue-mix viscosity. Finer particles produce higher viscosity due to larger area exposed to wetting medium during mixing.
3. Drying condition contributes different viscosity behavior. This factor does not act similarly as in the filler characteristic analysis.
4. Glue-mix viscosity are affected by types of filler added into the system. Tea waste shows its more hydrophilic characteristic than kemiri and white clay by developing high initial viscosity.

Recommendations

1. Kemiri shell is the most preferable filler material due to its moderate water filler ratio.
2. A study of the availability of these fillers and their constant supplies, their econimical aspects is still needed.

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